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B/Ca ratios in coccoliths and relationship to calcification vesicle pH and dissolved inorganic carbon

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Coccolithophorid algae are microscopic but prolific calcifiers in modern and ancient oceans. Different species and strains have exhibited diverse calcification responses to laboratory ocean acidification experiments. This hampers our ability to predict future alteration of marine biogeochemical cycles. It is unclear why their intracellular biomineralization is variably affected by extracellular seawater pH. B/Ca in abiogenic calcites increases at higher pH because only borate ion is incorporated into the calcite lattice, relative to boric acid which is the dominant species of B at lower pH. B/Ca ratios therefore are a potential indicator of pH shifts in the coccolith vesicle where calcification occurs. We used SIMS ion probe to measure B/Ca ratios of coccoliths from three different strains of Emiliania huxleyi and one strain of Coccolithus braarudii braarudii cultured under different seawater pH conditions to ascertain if B/Ca might elucidate the processes of coccolithophorid response to ocean acidification. These data are interpreted with the aid of a model for cellular boron acquisition by coccolithophorids. Based on uptake in other plants, we infer that boron uptake by cells is dominated by passive uptake of boric acid across the lipid bilayer. Subsequently in the alkaline coccolith vesicle (C.V.) boron speciates into borate and boric acid according to the C.V. pH, and borate is incorporated into the calcite of the coccolith. At increasing seawater pH, the boric acid abundance in seawater decreases, lowering the potential B flux into the cell. Homeostais or constant pH of the coccolith vesicle results in decrease of B/Ca ratios with increasing seawater pH . In contrast, if coccolith vesicle pH increases with increasing seawater pH, then B/Ca ratios will increase as the fraction of borate in the coccolith vesicle increases. The coccolith B/Ca ratio is also expected to depend inversely on the dissolved inorganic carbon (DIC) concentration in the coccolith vesicle. The B/Ca in cultured coccoliths is much lower than that of foraminifera or corals and limits precision in the analysis. Modest variations in DIC or pH of the coccolith vesicle can account for the observed ranges of B/Ca ratios in cultured coccoliths. The model shows that paired measurements of B/Ca and B isotopic composition of the calcite could distinguish between regulation of pH or DIC in the coccolith vesicle. In E. huxleyi the strains with high calcification rates have much higher B/Ca ratios than experiments, high calcification rates correspond to high B/Ca ratios in coccoliths, suggestive of higher coccolith vesicle pH favoring more rapid calcification.